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<b>(21) International Application Number:</b> PCT/US96/14793 <b>(22) International Filing Date:</b> 11 September 1996 (11.09.96) <b>(30) Priority Data:</b> 08/526,976 12 September 1995 (12.09.95) US <b>(71) Applicant (for all designated States except US):</b> KATALEUNA GMBH [DE/DE]; Am Haupttor, D-06236 Leuna (DE). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> ALBERS, Edwin, W. [US/US]; 596 Severn Road, Severna Park, MD 21146 (US). BURKHEAD, Harry, W., Jr. [US/US]; 5528 Willys Avenue, Baltimore, MD 21227 (US). MCDANIEL, J., Gary [US/US]; 108 Glenmore Court, Bel Air, MD 21014 (US). <b>(74) Agents:</b> STEINER, Arthur, J. et al.; Lowe, Price, Leblanc & Becker, Suite 300, 99 Canal Center Plaza, Alexandria, VA 22314 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
<b>(54) Title:</b> CATALYST AND APPLICATION FOR SAME		
<b>(57) Abstract</b> <p>A catalyst composition for a catalyst that can be used in petroleum refineries to aid in the cracking or conversion of hydrocarbons is disclosed. This catalyst is a composition that includes the incorporation of an active mineral component in conjunction with a conventional synthetic zeolite component. The discovery is the synergistic effects of this unique combination. The preferred embodiment is a catalyst containing clinoptilolite in conjunction with USY zeolite. Also disclosed is the catalyst's application in both fluid bed, fixed bed, and ebullating bed processes such as petroleum refinery FCC and hydrocracking units.</p>		

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## CATALYST AND APPLICATION FOR SAME

BACKGROUND OF THE INVENTION1. Field of the Invention

This invention relates to a catalyst and its use in petroleum refinery processes. The preferred embodiment of this invention relates to a fluid catalytic cracking ("FCC") catalyst known as an octane enhancement additive that is used to improve the octane of the FCC gasoline and to increase the yield of light olefins from the FCC unit. These light olefins are used as feedstocks to other processing units in the refinery such as the alkylation, MTBE, and TAME units as well as to downstream petrochemical plants. For example, the MTBE and TAME units use some of these olefins to produce the blending components which are used to make reformulated gasoline ("RFG").

2. Description of the Background Art

U.S. Patent Numbers 3,140,249; 3,140,243; 3,210,267; 3,271,418; 3,436,357; and 3,459,680 to Plank and Rosinski disclose molecular sieve (or zeolite) type FCC cracking catalysts. The world-wide petroleum refining industry rapidly adopted the use of these catalysts in the early 1960's because these catalysts provided for large improvements in FCC unit performance including significant improvements in gasoline yields and coke selectivity when compared to the previously used amorphous silica-alumina catalysts.

Elsewhere in the refinery the utilization of zeolite-based catalysts has also increased significantly. Synthetic zeolites have found their way into the formulations of numerous catalysts including those for hydrocracking, selectoforming, hydroisomerization, dewaxing, benzene alkylation, xylene isomerization, and methanol to gasoline conversion.

With the introduction in the late 70's of automotive catalytic converters to reduce exhaust emissions, refiners have had to virtually eliminate the use of lead in gasoline. Lead was used by refineries to increase the octane of the gasoline. As such, refiners have had to look for other methods to increase octane. Hence, FCC octane enhancement additives utilizing Mobil's patented ZSM-5 zeolite technology were introduced into the refining industry.

With the Clean Air Act ("CAA") amendments of 1990, the use of octane enhancement additives has increased significantly. The CAA amendments specify a formula for reformulated gasoline which includes the use of oxygenated materials, thus allowing the gasoline to burn cleaner. The main source of precursors (olefins) for these oxygenates is the FCC unit in the refinery. It has turned out that these ZSM-5 containing FCC additives are currently one of the best available commercial technologies to increase the yield of these olefins.

As the use of "pure" synthetic zeolites for refinery applications has taken off since the 1960's, the use of less selective silica-alumina catalysts and "less pure" natural zeolites declined rapidly. Today, the use of these materials is only found in obscure processes or in technologically backward refineries such as some of those found in the old Eastern-bloc countries.

One of the major reasons for the decline in the use of natural zeolites in refinery applications is the variability in quality that is found from source to source and even from the same source. Material that is mined from one area of a deposit is often quite different than material that is mined from another area of the same deposit. Synthetic zeolites, on the other hand, can be controlled during their manufacture so that one batch looks just like the next batch. As a result, the catalysts that are manufactured using synthetic zeolites

have both consistent properties and, more importantly, consistent performance.

Although mostly abandoned, however, one should not forget that the natural zeolites have some interesting structural characteristics that can provide many unique selectivity benefits to the refining industry. The challenge, of course, is to utilize these materials in such a way as to manufacture a "modern" catalyst with consistent properties and consistent performance.

The catalyst we have discovered is a petroleum refinery catalyst. This catalyst, which contains an active mineral component, is used to aid in the cracking or conversion of hydrocarbons in various refinery processes. The preferred embodiment of this invention is an FCC catalyst. This FCC catalyst is a new FCC octane enhancement additive that does not contain the ZSM-5 zeolite. It does, however, provide similar operational functionalities and performance as the ZSM-5 containing additives with respect to both conversion and selectivity, and particularly with respect to increasing light olefin yields.

#### SUMMARY OF THE INVENTION

The invention is a catalyst composition. The composition includes the addition of an active mineral component to the catalyst in conjunction with a conventional synthetic zeolite component. The discovery is the synergistic effects of this unique combination. Desirable active mineral components include natural zeolites and specialty clays. The preferred embodiment of this invention is a composition containing the natural zeolite clinoptilolite in conjunction with ultrastable-Y ("USY") zeolite.

The invention is also the use of this catalyst in petroleum refineries. In particular, this composition has application in all of the refinery's cracking processes

such as the FCC and hydrocracking processes. The catalyst is used in these processes to affect changes in their performance, particularly with respect to conversion and selectivity. In the preferred embodiment of this invention, the catalyst is used to increase the gasoline octane and to increase the yield of light olefins in the FCC unit.

#### DETAILED DESCRIPTION OF THE INVENTION

The invention is a catalyst composition for a catalyst that is used to aid in the conversion of hydrocarbons in petroleum refinery processes. For example, in the preferred embodiment of this catalyst, a synergistic blend of USY zeolite and clinoptilolite natural zeolite, the catalyst is used to increase the gasoline yield and octane and to increase the yield of light olefins in the refinery's FCC unit.

The catalyst composition can take many forms depending upon the application and the desired catalytic selectivities. What is important is the inventors recognition of the synergistic effects of multiple-zeolite catalyst systems.

The catalyst composition first must contain an active mineral component. Desirable active mineral components include natural zeolites such as clinoptilolite, chabazite, erionite, ferrierite, gmelinite, heulandite, mordenite, offretite, phillipsite, sodalite, stilbite, thomsonite, and mixtures thereof. The preferred embodiment of this invention contains the natural zeolite clinoptilolite.

When mined, many active minerals often have very low surface areas. This is due in large part to entrapped or occluded "debris" within the mineral's structure that blocks access to the internal surfaces of the material. To obtain the maximum catalytic effects of these materials, therefore, it is often necessary and desirable

to remove this debris prior to the incorporation of the active mineral into the catalyst. This is accomplished through an acidic or basic leaching of the material. The procedures for performing such leachings are commercially practiced and will not be discussed here. Acidic or basic leaching is selected depending upon the nature of the debris that is to be removed and to some extent upon the catalyst that is to be made.

The catalyst composition must also include a synthetic zeolite. It is this zeolite that provides the controllability or "steady hand" to the catalytic performance of the overall catalyst in the FCC unit. The active mineral component supplying the something extra that the synthetic zeolite cannot provide on its own. Desirable synthetic zeolites are Na-A, Ca-A, K-A, Na-X, Na-Y, HY, USY, ZSM-5, LZV-210, and mixtures thereof. In addition, variations of these zeolites such as the rare earth exchanged Y zeolites are also desirable. The preferred embodiment of this invention contains USY zeolite.

We have also found that this synthetic zeolite component can be omitted from the catalyst composition in its entirety depending on the yield selectivities desired from the FCC unit. The synergistic effects of the active mineral component with the synthetic zeolite can still be observed, however, because of the presence of a synthetic zeolite in the FCC catalyst itself. The intimate mixing of FCC catalyst and additive that occurs in the circulating inventory of the FCC unit allows the synergistic effects to occur. However, the magnitude of the effects are reduced to some extent. This is believed to be the result of diffusional limitations due to the fact that these two active components do not exist in the same fluid particles.

The catalyst composition also includes the incorporation of a clay component for binding and/or as

a filler. Desirable clays include bentonite, calcined kaolinite, kaolinite, metakaolin, montmorillonite, chlorite, talc, and mixtures thereof. The preferred embodiment of this invention contains kaolinite clay.

5           And finally, the catalyst composition includes a binder component to "glue" the components together into the particles that are the catalyst. Depending on the application, different binding systems are used. For example, in more severe, high temperature applications  
10       such as FCC, a hydrothermally stable inorganic binder such as aluminum chlorohydrate or peptized alumina is used. Desirable inorganic binders include sols of aluminum such as aluminum chlorohydrate, peptized aluminas, sols of silica, colloidal silicas, sols of  
15       titanium, sols of zirconium, clays such as bentonite, calcined kaolinite, kaolinite, metakaolin, montmorillonite, chlorite, and talc, and mixtures of these. Desirable concentrations of inorganic binders are from about 2 to about 15 weight percent.

20           Numerous surfactants can be used in the catalyst composition of this invention as well. A surfactant is initially selected for its stability in the component to which it is added. For example, the surfactant can be added to numerous "streams" that are used in the process  
25       of this invention. A stream is often a slurry of a component used to form the desired particle. A stream can also be a dry component. If a stream, within which a surfactant is to be added, is acidic or alkaline, a surfactant must be chosen that is stable in the pH of the  
30       selected stream. The surfactants are used primarily to enhance the manufacturing process when making the catalyst. Surfactants aid in the dispersion of the individual component particles that make up the catalyst and provide for particles that have superior density and  
35       hardness characteristics. Desirable surfactants include anionic fluorohydrocarbon materials. A suitable

concentration of surfactant is desirably between 0.25 and 4 grams per 5 kilograms of dried product.

This invention is also the use of a catalyst with this composition to aid in the conversion of hydrocarbons in petroleum refineries. Two such processes are the FCC process and the hydrocracking process.

In the FCC process, the invented catalyst, in this case known as an FCC additive, is added to the FCC unit in the same manner as the cracking catalyst that is being used. It can be added separately or together in a mixture with the cracking catalyst. Usually the addition is accomplished by using a pneumatic conveying system to blow the material(s) directly into the FCC regenerator. The catalyst additive then circulates through, the FCC unit in direct contact and along with the FCC catalyst. The quantity of FCC additive that is added and which then circulates in the unit must be sufficient to effectively change the catalytic selectivity of the unit when compared to the selectivity of the base FCC catalyst being used. Therefore, an FCC additive level of between 0.5 and 25.0 percent of the circulating FCC inventory is desirable.

The FCC additive we have discovered utilizes the unique synergies of clinoptilolite and USY zeolite to increase the octane of the gasoline and increase the yield of light olefins that are produced in the FCC unit.

#### EXAMPLES

The following Examples represent the composition and process of the invention.

#### COMPARATIVE EXAMPLES A & B

The catalysts of Comparative Examples were obtained commercially. Their exact formulations and the procedures for preparing them are proprietary.

The catalyst of Comparative Example A is sold under the trade name AMOCO EQ by the Amoco Oil Company. The AMOCO EQ catalyst represents a standard USY zeolite containing octane catalyst.

The catalyst of Comparative Example B is the AMOCO EQ catalyst blended with a commercially available FCC octane enhancement additive ("Z-ADD") containing Mobil's patented ZSM-5 zeolite. The FCC octane enhancement additive used contains 25 wt.% ZSM-5 zeolite. The AMOCO EQ and Z-ADD are blended to a 90:10% ratio. This ratio represents a typical commercial FCC catalyst to FCC octane enhancement additive level.

The catalyst of the Comparative Examples were tested in a microactivity test ("MAT") unit under standard ASTM conditions. The MAT test is used to simulate the performance of the catalysts in a commercial FCC unit. The MAT data for the Comparative Examples is presented in Table 1 below:

TABLE 1

Steam Condition is 1450°F for 5 hours		<u>Comp. Ex. A</u>	<u>Comp. Ex. B</u>
C/O		3.02	2.96
WHSV		15.89	16.23
Conversion, wt. %		53.91	50.97
<u>Yields, wt. %</u>			
Hydrogen		0.07	0.10
C1		0.59	0.55
C2		0.55	0.51
C2=		0.56	0.51
C3		1.03	0.91
C3=		3.68	4.62
IC4		3.09	2.96
NC4		0.58	0.58
C4=1		0.89	1.07
IC4=		1.31	1.84
T-C4=		1.17	1.46
C-C4=		0.84	1.04
C5+ Gasoline		34.89	33.10
LCO		23.84	21.93
HCO		22.25	27.11
Coke		4.60	1.72

EXAMPLES 1 and 2

The catalysts of Examples 1 and 2 are suitable for use as octane enhancement additives in the FCC process and are prepared according to the general procedures as described below:

GENERAL PROCEDURE

The following general procedure was used in making the catalysts of the Examples of the invention:

1. A "silica sol" binder solution is prepared consisting of acidified aluminum sulfate ("acid/alum") and sodium silicate as follows:

A quantity of 0.454 kilograms ("kg") of aluminum sulfate ("alum") is mixed with 1.79 kg of water. The mixture is agitated thoroughly until all of the alum is dissolved. After the alum solution is ready, 0.029 kg of 95% to 98% sulfuric acid is added. The solution is then cooled to at least 86°F (30°C) before it is used. The acid/alum solution is pumped into a high shear mix pump simultaneously with a pumped stream of sodium silicate containing 12.4 wt.% silica. The silicate flow rate is adjusted to achieve a pH in the mixing pump discharge in the range of 2.80 to 3.05 pH. A 3:1 flow of silicate to acid/alum is typically required to achieve the desired pH.

2. A clay slurry is prepared as follows:

A slurry of kaolin clay is made up to a 70% solids slurry, measured by O'Haus moisture balance, using the dispersing agents tetrasodium pyrophosphate ("TSPP") and sodium polyacrylate ("NaPa"), in a slurry make-up water. The proportions used are 0.24% TSPP predissolved in hot water to a 10% solution, and 0.25% NaPa, based on the weight of the air float kaolin clay. The dispersants are

first added to the make-up water followed by the dry clay which is added under high shear agitation.

5 3. A zeolite slurry of the zeolite(s) to be used is prepared by slurrying dry zeolite powder(s) in water to 30% solids. The pH of the slurry is adjusted to 4.5 to 4.8 pH using 20% sulfuric acid.

4. The required amount of the binder solution is transferred to a mix tank under a high shear mixer. The temperature and pH of the mixture are recorded.

10 5. The required amount of the clay slurry is added to the binder solution in the high shear mix tank. The temperature and pH of the mixture are recorded.

15 6. The required amount of zeolite slurry is then added to the high shear mix tank. The temperature and pH of the mixture are recorded.

20 7. This mixture is then pumped to an Anhydro Model Type III-A No. 4 spray dryer employing a spinning wheel atomizer. Operating conditions are, 650°F (343°C) inlet temperature, 250°F (121°C) outlet temperature, and 10,000 rpm atomizer wheel speed.

8. The spray dried product is then ion exchanged with an ammonium solution to remove undesirable sodium, washed with water, and then dried.

25 The catalyst additives of these Examples are then blended with the AMOCO EQ catalyst at a 90%:10% ratio of AMOCO EQ to Example additive. This is the same blend ratio as the AMOCO EQ to Z-ADD ratio in Comparative Example B. The microactivity test data of these examples,

therefore, is directly comparable to the data of the Comparable Examples.

#### EXAMPLE 1

This example represents the preferred embodiment of the invention. The catalyst was formulated to contain 15 weight percent clinoptilolite as the active mineral component; 10 weight percent USY zeolite as the synthetic zeolite component; 20 weight percent silica sol binder; and the balance, 55 weight percent kaolin clay.

#### Example 2

This Example provides an octane enhancement additive containing an active mineral component but with no synthetic zeolite component. However, when added to an FCC unit this additive is closely intermixed with the FCC catalyst (which contains a synthetic zeolite as its active component) in the FCC unit's circulating inventory. In this situation, the synergies between the active mineral component of the additive and the synthetic zeolite of the catalyst can still be observed. The catalyst additive of this example contains 25 weight percent clinoptilolite; 20 weight percent silica sol binder; and the balance, 55 weight percent kaolin clay.

The MAT data for the Examples is presented in Table 2 below:

TABLE 2

	<u>Example 1</u>	<u>Example 2</u>
Steam Condition is 1450°F for 5 hours		
C/O	3.01	3.07
WHSV	15.93	15.63
Conversion, wt. %	56.97	56.20

		<u>Example 1</u>	<u>Example 2</u>
	Steam Condition is 1450°F for 5 hours		
	Yields, wt. %		
<u>5</u>	Hydrogen	0.13	0.15
	C1	0.70	0.80
	C2	0.63	0.73
	C2=	0.61	0.66
	C3	0.95	1.21
<u>10</u>	C3=	4.23	4.43
	IC4	2.66	3.15
	NC4	0.63	0.67
	C4=1	0.98	1.08
	IC4=	1.83	1.81
<u>15</u>	T-C4=	1.32	1.45
	C-C4=	0.95	1.04
	C5+ Gasoline	39.60	35.70
	LCO	24.93	22.29
	HCO	18.10	21.51
<u>20</u>	Coke	1.75	3.31

As can be seen, the additive of Example 1, a combination of USY zeolite and clinoptilolite, shows remarkable synergistic effects. The gasoline and light cycle oil yields are much higher than that of the USY zeolite containing catalyst of Comparative Example A or of the clinoptilolite containing additive system of Example 2. In addition, the increase in the yield of light olefins is greater than one would have expected if one interpolated the data between these two extreme cases.

In addition, the additive containing clinoptilolite in Example 2 provides similar yields and selectivities as the commercial ZSM-5 containing additive. This is due to a large part to the synergistic effects of the clinoptilolite with the USY zeolite in the AMOCO EQ catalyst. Clinoptilolite does not provide such functionality on its own.

We claim:

1. A process for the selective cracking of petroleum feedstocks in a petroleum refinery catalytic cracking unit operating at processing conditions comprising introducing into said fluid catalytic cracking unit a crude hydrocarbon, a fluid catalytic cracking catalyst and a composition comprising a mixture of a USY synthetic zeolite and clinoptilolite natural zeolite whereby there is an increase in the yield of light olefins and tertiary butyl hydrocarbons.

2. A process as in claim 1 wherein said composition contains a clay.

3. A process as in claim 2 wherein said clay is selected from the group consisting of bentonite, calcined kaolinite, kaolinite, metakaolin, montmorillonite, chlorite, talc and mixtures thereof.

4. A process as in claim 2 wherein said composition contains a binder.

5. A process as in claim 4 wherein said binder is selected from the group consisting of sols of alumina, sols of silica, sols of titania, sols of zirconia, clays and mixtures thereof.

6. A process as in claim 5 wherein said clay is selected from the group consisting of bentonite, calcined kaolinite, kaolinite, metakaolin, montmorillonite, chlorite, talc and mixtures thereof.

7. A process for the selective cracking of petroleum feedstocks in a petroleum refinery catalytic cracking unit operating at process conditions comprising

introducing into said fluid catalytic cracking unit a crude hydrocarbon, a fluid catalytic cracking catalyst containing USY synthetic zeolite catalyst and a clinoptilolite natural zeolite composition whereby there is an increase in the yield of light olefins and tertiary butyl hydrocarbons.

8. A process as in claim 7 wherein said composition contains a clay.

9. A process as in claim 7 wherein said clay is selected from the group consisting of bentonite, calcined kaolinite, kaolinite, metakaolin, montmorillonite, chlorite, talc and mixtures thereof.

10. A process as in claim 7 wherein said composition contains a binder.

11. A process as in claim 10 wherein said binder is selected from the group consisting of sols of alumina, sols of silica, sols of titania, sols of zirconia, clays and mixtures thereof.

12. A process as in claim 11 wherein said clay is selected from the group consisting of bentonite, calcined kaolinite, kaolinite, metakaolin, montmorillonite, chlorite, talc and mixtures thereof.

13. A process for the selective cracking of petroleum feedstocks in a petroleum refinery fluid catalytic cracking unit operating at processing conditions comprising introducing into said fluid catalytic cracking unit a crude hydrocarbon, a fluid cracking catalyst comprising a mixture of USY synthetic zeolite and a natural zeolite whereby there is an increase in the yield of light olefins and tertiary butyl hydrocarbons.

14. A process as in claim 13 wherein said natural zeolite is selected from the group consisting clinoptilolite, chabazite, erionite, ferrite, gmelinite, heulandite, mordenite, offretite, phillipsite, sodalite, stilbite, thomsonite and mixtures.

15. A process as in claim 13 wherein said catalyst contains a clay.

16. A process as in claim 15 wherein said clay is selected from the group consisting of bentonite, calcined kaolinite, kaolinite, metakaolin, montmorillonite, chlorite, talc and mixtures thereof.

17. A process as in claim 13 wherein said catalyst contains a binder.

18. A process as in claim 17 wherein said binder is selected from the group consisting of sols of alumina, sols of silica, sols of titania, sols of zirconia, clays and mixtures thereof.

19. A fluid catalytic cracking catalyst for the enhanced yield of light hydrocarbons and tertiary butyl hydrocarbons comprising a USY synthetic zeolite and clinoptilolite natural zeolite.

20. A fluid catalytic cracking catalyst as in claim 19 wherein said catalyst includes a clay.

21. A fluid cracking catalyst as in claim 20 wherein said clay is selected from the group consisting of calcined kaolinite, kaolinite, metakaolin, montmorillonite, chlorite, talc and mixtures thereof.

22. A fluid cracking catalyst as in claim 19 wherein said catalyst contains a binder.

23. A fluid cracking catalyst as in claim 22 wherein said binder is selected from the group consisting of sols of alumina, sols of silica, sols of titania, sols of zirconia, clays and mixtures thereof.

24. A fluid cracking catalyst for the enhanced yield of light olefins and tertiary butyl hydrocarbons comprising a USY synthetic zeolite and an amount of a natural zeolite effective to increase the yield of light olefins and tertiary butyl hydrocarbons.

25. A fluid cracking catalyst as in claim 24 wherein said natural zeolite is selected from the group consisting of clinoptilolite, chabazite, erionite, ferrite, gmelinite, heulandite, mordenite, offretite, philipsite, sodalite, stilbite, thomosonite and mixtures thereof.

26. A fluid cracking catalyst as in claim 24 wherein said catalyst contains a clay.

27. A fluid cracking catalyst as in claim 26 wherein said clay is selected from the group consisting of calcined kaolinite, kaolinite, metakaolin, montmorillonite, chlorite, talc and mixtures thereof.

28. A fluid cracking catalyst as in claim 24 wherein said catalyst contains a binder.

29. A fluid cracking catalyst as in claim 28 wherein said binder is selected from the group consisting of sols of alumina, sols of silica, sols of titania, sols of zirconia, clays and mixtures thereof.

30. In a process of selective cracking of petroleum feedstocks in a petroleum refinery FCC unit containing a synthetic zeolite, the improvement comprising supplying an FCC additive to said synthetic zeolite- containing FCC unit to increase the octane of FCC gasoline and yield of light olefins, the FCC additive comprising a clinoptilolite natural zeolite.

31. The process of claim 30 wherein the FCC additive is a mixture of the clinoptilolite natural zeolite, a clay and a binder.

32. The process of claim 31 wherein the mixture supplied to said synthetic zeolite-containing FCC consists essentially of the clinoptilolite natural zeolite, a clay and a binder.

33. An FCC additive for use in a synthetic zeolite-containing FCC unit comprising clinoptilolite natural zeolite.

34. The FCC additive of claim 33 further comprising a mixture of the clinoptilolite natural zeolite, a clay and a binder.

35. The FCC addition of claim 34 wherein the mixture consists essentially of clinoptilolite natural zeolite, a clay and a binder.

36. The FCC catalyst composition comprising:  
a synthetic zeolite and a clinoptilolite natural zeolite.

37. The FCC catalyst composition according to claim 36 wherein the clinoptilolite natural zeolite constitutes an octane enhancement addition.

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US96/14793

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) : C10G 11/05; B01J 29/08, 29/80

US CL : 208/113, 120; 502/67, 68, 79

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 208/113, 120; 502/67, 68, 79

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

STN - apipat, apilit: search terms: fluid catalytic cracking, zeolite y, catalyst, clinoptilolite

APS - search terms: usy, clinoptilolite, fcc, catalytic cracking

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ----- Y	ZA 8806732 A (G. HUTCHINGS) 30 May 1989 (30-05-89), Abstract only, see entire abstract.	1, 7, 13, 14, 19, 24, 25, 30, 33, 36, 37 ----- 2-6, 8-12, 15- 18, 20-23, 26- 29, 31, 32, 34, 35
Y	US 3,758,403 A (ROSINSKI ET AL) 11 September 1973 (11- 09-73), col. 7, line 63 through col. 8, line 5.	2-6, 8-12, 15- 18, 20-23, 26- 29, 31, 32, 34, 35

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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